Thermal Transport Property Measurements of Coatings, Thin Films and Contact Conductance¹

R.E. Taylor²

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² Thermophysical Properties Research Laboratory, Inc., 2595 Yeager Road, West Lafayette, IN 47906, U.S.A.

ABSTRACT

There is an intense and growing demand for knowledge of the thermal transport properties of coatings, thin films and contact conductances. The measurement of these properties is considerably more difficult than those for larger specimens. These difficulties are associated with the uncertainties and non-uniformity of sample thickness, gradations in the properties of very thin films, and contact conductance between the coating and substrate. Also the problem is two-dimensional as the properties of the coatings are unlikely to be the same in the in-plane and through-thickness directions. When one adds the complications arising with measurements over extended temperature ranges to these considerations, the desirability of using a variety of techniques becomes evident.

KEY WORDS: adhesives; coatings; contact conductance; thermal barrier coatings; thermal conductivity; thin films

INTRODUCTION

Thermal transport properties of thin coatings such as thermal barrier coatings (TBC's) used in airplane engines and other thin films present special challenges to the researcher. These difficulties arise from extreme sensitivities associated with uncertainties and non-uniformity of sample thickness, possible gradations in properties of very thin films, contact conduction between coating and substrate and the general problems of dealing with small or fragile samples. When one adds the complications of measuring over very wide temperature ranges and 2-D properties, the necessity of having a variety of techniques becomes evident.

2. Laser Flash Technique

The laser flash method [1] to measure diffusivity (α) combined with differential scanning calorimetry (DSC) to measure specific heat (C_p) and bulk density (ρ) values calculated from sample geometry and mass has been an effective method to determine thermal conductivity (λ). Thermal conductivity values are calculated as the product of these quantities, i.e. $\lambda = \alpha C_p \rho$. This approach enjoys the advantages of using small samples of simple shapes, ability to measure over wide temperature ranges rapidly (and hence being cost-effective) and enjoys a relatively high degree of accuracy when properly performed with suitable geometry samples.

The laser flash method, ASTM E 1461-92 involves holding a sample, normally the size of a nickel, at the desired measurement (e.g., room temperature, 100°C, 200°C, etc.). The front surface receives a pulse of energy from the laser, which soon raises the back face temperature a degree or two. The rear face temperature response is normalized and compared with the theoretical model based on Carslaw and Jaeger's solution to one-dimensional heat flow [2]. Using that model, diffusivity values can be obtained at any percent rise of the curve.

Layered structures have been studied extensively, [3, 4, 5]. The dimensionless rear-face

temperature-rise history following an instantaneous heat pulse to the front of a layered sample composed of layers whose diffusivity ratios are less than about 10:1 is the same as that for a homogeneous sample, provided there is no contact resistance between the layers.

H. J. Lee and Taylor [4] and Lee et al [3] developed computer programs which calculate the thermal diffusivity of one layer of a two-layer or three-layer composite from the half-time, $t_{1/2}$, measured in the conventional manner by the flash technique. Programs were also written and tested to compute the contact conductance between two layers whose thermal properties are known. Lee et al [3] also established the criteria for distinguishing between a resistive and a capacitive layer. It is interesting to note that reversing the direction of heat flow does not affect the response curve.

3. Experimental Results Obtained by the Flash Technique

3.1 Thermal Barrier Coatings

Even though samples of free-standing TBC's have been measured, it was often necessary to add thin coatings to the front surface to prevent laser beam penetration. In addition, we usually had to apply a very thin coating on the rear surface to prevent our i.r. detector from viewing into the sample and thus not giving an accurate temperature rise curve for the rear surface. In general, the presence of a rear surface coating did not have to be accounted for because it only takes a very thin layer to prevent the i.r. detector from viewing into the sample interior. However, preventing a relatively severe laser burst from penetrating into the samples may require a significant protective coat, depending upon the translucency of the TBC. In cases of a substantial front layer, the presence of the protective coat must be accounted for and the experiment becomes a two-layer case (see below). It should be noted that in the case of TBC's mounted on a metal substrate, there is no need for a protective front layer, since the metal substrate provides this, i.e. we always have the substrate side positioned towards the laser.

The agreement in the conductivity values for TBC samples of 17 and 56 mil thicknesses was generally within 4%, even though the half-time values were almost a factor of ten different [6]. This is a strong indication that the results are valid (along with on-line comparisons of experimental to theoretical rise curves) and that the translucency problem is in hand.

While we routinely determine the thermal conductivity of one layer bonded to another, the accuracy strongly depends upon the absolute and relative values of the individual layers. The input parameters which enter into a two-(or three) layer calculation are the thicknesses, densities and specific heat of each layer, the diffusivity of one (or two) layers, and the measured half rise times. The sensitivity of each of these parameters also depends on the relative values between these parameters for the various layer, i.e. the relative magnitudes of the layer thicknesses, the relative magnitudes of the diffusivity/conductivity values, etc. The situation is further complicated by the fact that the calculations of the diffusivity/conductivity value of the unknown layer is based upon parameter estimation (i.e. iterative) procedures. Therefore several cases we were faced with experimentally were examined. These cases all involve superalloy substrates whose conductivity/diffusivity values increased substantially with increasing temperature and TBC's of relatively low diffusivity/conductivity values which were relatively temperature-independent. This means that the relative magnitudes of the diffusivity/conductivity values for the substrate and coating increases substantially with increasing temperature. For example, the conductivity ratios of substrate to coating were of the order of 10:1 at 100°C and greater than 20:1 at 1000°C.

The effects of uncertainties in the input parameters for the case of a 11 mil coat bonded to a 25 mil substrate at 500°C are examined in Figure 1 [6]. The calculated conductivity values are most sensitive to the uncertainty in the coating thickness and the measured half-times. However, it should be possible to obtain sufficiently accurate input parameter values to obtain reasonable results for this

case.

However, when we consider a 3.3 mil coat on a 120 mil substrate at 500° C (Fig. 2) [6], the extreme sensitivities of the calculated conductivity value to errors in substrate thickness, diffusivity and to half-rise times precludes meaningful results. For example, a $\pm 1\%$ change in the value assigned to substrate thickness results in changes of +60 and -28% change in the conductivity values. A $\pm 2\%$ change in the measured half-time value from 0.34089 seconds (i.e. 0.34087 ± 0.00682 sec) results in change in the calculated conductivity values of +65 to -30%.

As mentioned earlier, these sensitivities also depend upon the relative magnitudes of the diffusivity/conductivity values of the substrate and TBC. The bigger this ratio, the better the experiment. This is the reason that the conductivity values for the layered composites approach those for the free-standing coatings at higher temperatures. It is interesting to note that coating conductivity values could be determined fairly accurately under the conditions of Figure 2 if their values were one-tenth of the value normally encountered.

To summarize our experiences with the laser flash technique applied to TBC coatings, we routinely obtain very good results for 20 mil coatings, fair results for 10 mil coatings and fair to terrible results for 5 mil or thinner coatings, depending upon the manufacturer's ability to furnish accurate information on layer thicknesses and densities.

3.2 Paints, Adhesives and Greases

We have measured hundreds of samples of paints, adhesives, greases or scales on substrates. Again, we must know the properties of the substrate and the layer thicknesses accurately in order to get reliable results. We must also take precautions to insure that the i.r. detector does not view into the sample. The measurement of the conductivity of paints, whose values often lie in the 0.002 to 0.006 W cm⁻¹K⁻¹ range, have not proven to be very difficult.

Many customers have attempted to increase the conductivity of adhesives and greases by adding particles of high conductivity. Invariably they have been very disappointed to find out that the rule of mixtures does not apply, i.e. they thought that adding 25% particles of a high conductivity material to the adhesive or grease would cause the conductivity of the mixture to be about 25% that of the high conductivity particles. There are numerous equations to predict the conductivity of such two-phase systems [7]. We often found the Bruggeman-variable dispersion equation to be the best [8]. However, the actual increase in conductivity is also dependent upon such factors as particle shape and size, particle dependency to "clump" instead of disperse uniformly, etc.

3.3 Scales and Anodized Surfaces

The problems caused by scales have varied widely. In the case of rolling mills, for example, the effective conductivity was not appreciably altered by the formation of a scale on the rolling surface - probably because of the pressures and temperatures encountered. On the other hand, scales formed in the interior walls of pipes and heat exchanges have been found to have significant consequences.

A particular intriguing case involves anodized aluminum. We measured the case of a 0.006 inch thick anodized layer on a 0.157 inch thick aluminum alloy substrate. Based on our experiences with TBC's and other materials, we expected a difficult task. However, the results were very good as there were large differences between the measured half times for the substrate and substrate plus coating. It turns out that the conductivity of the anodized layer is only 0.011 W cm⁻¹K⁻¹ compared to 1.65 for the aluminum alloy - a factor of 150. In fact, the presence of the relatively thin anodized layer on the surface reduced the effective conductivity of the material by a factor of 8! The conductivity of anodized aluminum is much different from that associated with Al₂0₃. This is undoubtedly due to a large difference in structures of the two - as the large oxygen atoms interact

with the relatively small aluminum atoms in attempting to form a closest packing of oxygen spheres with aluminum atoms in the interstices. The ease in measuring this system compared to the diffusivity of measuring correspondingly thickness TBC layers on a superalloy support the statements made in that sections under sensitivity analysis, i.e. changing the conductivity ratio from 10:1 to 150:1 makes it easy to determine the conductivity values for the coatings.

3.4 Contact Conductance and Joints Between Dissimilar Members

When the properties of two layers are known, the contact conductance (H) between the layers can be determined using the laser flash technique [1]. An example of the normalized rear face temperature rise for a sample of silicon attached with grease to an aluminum heat sink compared to the perfect thermal contact between them is shown in Figure 3. It was quite easy to measure the increase in contact conductance (i.e. the decrease in interfacial resistance) with applied pressure. It must be remembered that conductance (ending in -ance) is not an intrinsic property (such as conductivity which ends in -ity). Thus, the thickness of the layers contribute to the magnitude of H and a simple statement that H is a certain value other than zero or infinity is not definitive. However, with the value of H, and the thicknesses and conductivities of each layer, the effective conductivity of the sample can be calculated.

4. Step Heating

The step heating technique involves flooding the front face of a sample with a constant or long time heat source and measuring the temperature response at the rear surface or at several locations [9, 10]. It has been successfully applied to insulations and large-grained materials, neither of which are very suited for the laser flash technique. We have modified the technique for use in studying high conductivity films in the in-plane direction [11]. In this case, the method is similar to the periodic techniques of Hatta, Sasuga, Kato and Maesono [12], except that the method is DC and uses

temperature rise curves as opposed to frequency shifts. The technique was checked using foil samples of tantalum, copper and molybdenum. The results on a CVD diamond film are shown in Figure 4. Data obtained with the four-probe method [13] and the data for GE [14] are also included in Figure 4. The peak values of sample A and sample B occur near 200 and 250 °K, respectively. The thermal conductivity of both sample roughly follows the T³ rule in the low-temperature region (below 200°K) where boundary phonon scattering is dominant. However, at relatively high temperatures, the thermal conductivity is relatively less sensitive to T and the boundary phonon scattering is less important. One observation from Figure 4 is that the thermal conductivity data at low temperatures follow the following sequence: GE sample > Sample A > Sample B. The peak values of each sample follow the reverse sequence. The grain scattering effect could be one explanation for this phenomenon. The SEM of samples A and B in Figure 4 shows that the grain sizes of sample A and sample B are about 20 and 2µm, respectively, and the grain size of the GE sample was reported to be 175µm. Phonon theory indicates that the effect of the smaller grain size will depress the conductivity at very low temperatures and shift the peak value to higher temperature. Another observation in Figure 4 is that the measured data of polycrystalline films approach the value for single crystal diamond [15] near room temperature, which indicates that boundary phonon scattering is not the dominant phenomenon in CVD diamond near room temperature. Umklapp processes dominate the phonon scattering in this temperature region.

5. Multiproperty Apparatus

This technique [16] involves Joulean heating of an electrically conducting sample enclosed in a vacuum system. Power generated in the central portion of the sample where temperature gradients are negligible are equated to heat losses. Electrical resistivity and total hemispherical emissivity values are calculated from measured voltage drops, current flow, sample geometry and

temperature. Recently, TBC coated thin walled metal tubes were examined. From the temperature gradient across the TBC coating, thermal conductivity values for the coating could be calculated. The conductivity values obtained were about half those usually encountered for TBC's of this chemical composition. However, the structure of the deposited TBC was deliberately different from the usual structure in such a manner that the conductivity should be considerably smaller. Thus, it appears that this technique may be a useful method to determine conductivity values for TBC's. However, additional studies are required before the method is put "on-line". The advantages of this technique include a linear dependence of conductivity on coating thickness rather than the quadratic dependence inherent in diffusivity methods, and the possibility of better effective averaging of uncertainties in thickness. The major disadvantage is the necessity of coating larger specimens and determining temperature gradients across the TBC.

6. Photo-Acoustic Techniques

We are investigating photo-acoustic techniques [17]. The obvious advantage of this approach is the elimination of a knowledge of coating thickness. The major disadvantage is the difficulty in covering an extended temperature range. We may use this technique to determine the values near room temperature and calculate the

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effective thickness of the layers for laser flash experiments.

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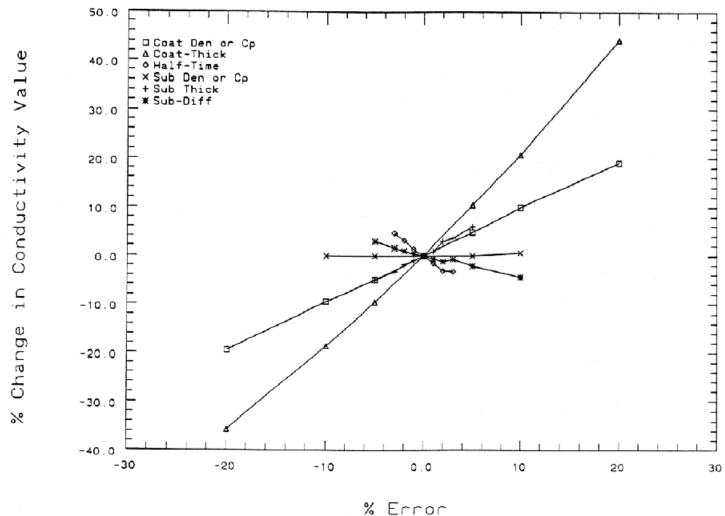
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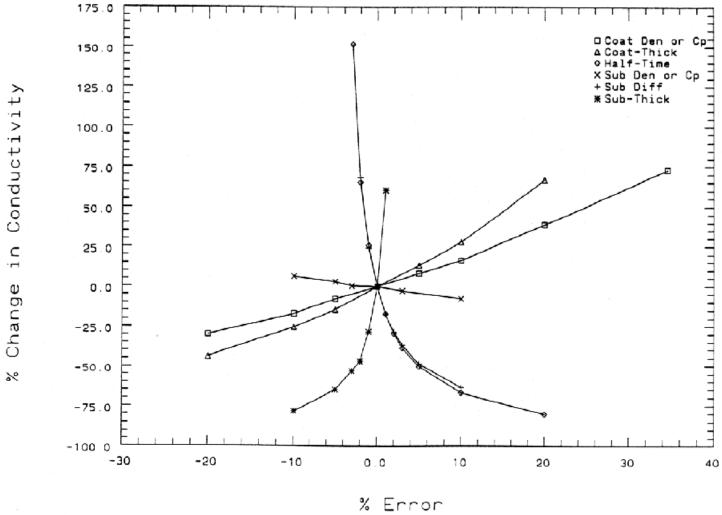
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FIGURE CAPTIONS

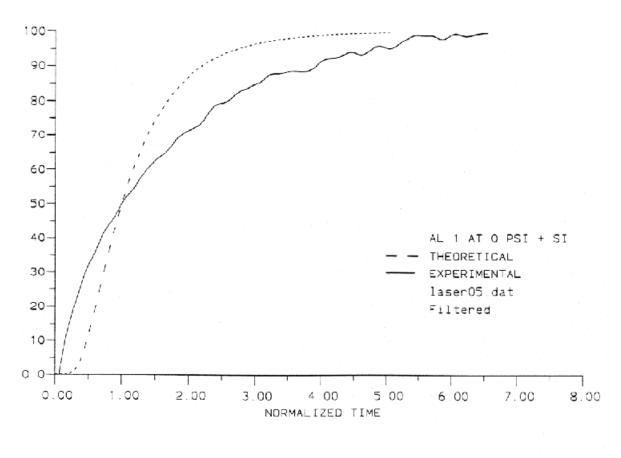
- Fig. 1. % Error (11 Mil Coat on 25 Mil Substrate)
- Fig. 2. % Error (3.3 Mil Coat on 120 Mil Substrate)
- Fig. 3. Comparison of Normalized Experimental versus Theoretical Rise Times (0 psi)
- Fig. 4. In-Plane Conductivity of Diamond Films



% Error
11 Mil Coat on 25 Mil Substrate



3.3 Mil Coat on 120 Mil Substrate



HALFTIME
BASELINE
MAXIMUM
TEMP

.2126063 .6145582 .9935943 150 SECONDS VOLTS VOLTS C THICKNESS : RUN ON :

.4896 CM 02-25-1997 11:53:30

